

## 镧系元素(La、Tb、Dy)的喹啉氧基乙酰胺配合物的结构及荧光性质

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**摘要:** 合成并通过单晶衍射表征了 3 个稀土配合物  $[\text{LaL}_2(\text{NO}_3)_3] \cdot \text{CH}_3\text{CN}$  (**1**),  $[\text{Ln}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})]$  ( $\text{Ln}=\text{Tb}$  (**2**),  $\text{Dy}$  (**3**),  $\text{L}=\text{N}$ -苯基-2-(5-氯-8-喹啉氧基)乙酰胺)。在配合物 **1** 中, 十二配位的  $\text{La}(\text{III})$  离子采取扭曲的二十面体配位构型, 分别与来自 2 个酰胺配体 **L** 的 4 个氧原子和 2 个氮原子, 及 3 个双齿配位硝酸根配位。配合物 **2** 和 **3** 的结构与拥有相同有机配体的  $\text{Pr}$ 、 $\text{Nd}$ 、 $\text{Sm}$ 、 $\text{Eu}$ 、 $\text{Gd}$  和  $\text{Er}$  配合物同构。在每个配合物中, 十配位的稀土离子与来自 1 个配体 **L** 的 2 个氧原子和 1 个氮原子, 3 个双齿配位硝酸根和 1 个水分子配位, 拥有扭曲的双帽四方反棱柱配位构型。固态配合物 **2** 和 **3** 在可见区发射强荧光。

**关键词:** 酰胺配体; 喹啉; 稀土配合物; 荧光; 晶体结构

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## Lanthanide(La, Tb, Dy) Complexes with Quinolinyloxy Acetamide Ligand: Crystal Structures and Fluorescence Properties

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**Abstract:** Three lanthanide(III) complexes,  $[\text{LaL}_2(\text{NO}_3)_3] \cdot \text{CH}_3\text{CN}$  (**1**),  $[\text{Ln}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})]$  ( $\text{Ln}=\text{Tb}$  (**2**) and  $\text{Dy}$  (**3**)) based on **L** ( $\text{L}=\text{N}$ -phenyl-2-(5-chloro-quinolin-8-yloxy)acetamide) have been synthesized and characterized by elemental analyses, IR spectra and X-ray diffraction analyses. The results reveal that the  $\text{La}(\text{III})$  ion in complex **1** is surrounded by two tridentate amide ligands with  $\text{NO}_2$  donor set and three bidentate nitrate anions, thus giving distorted icosahedron coordination geometry. By contrast, both complexes **2** and **3** are isostructural with those of the  $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ ,  $\text{Gd}$  and  $\text{Er}$  complexes bearing same ligand. In each complex, the center  $\text{Ln}(\text{III})$  ion with bicapped square antiprism coordination geometry is coordinated by one tridentate **L**, three bidentate nitrate anions and one water molecule. In addition, in solid state, complexes **2** and **3** could exhibit strong fluorescence emission in the visible region. CCDC: 1438578, **1**; 1438579, **2**; 1438580, **3**.

**Keywords:** amide type ligand; quinoline; lanthanide complex; fluorescence; crystal structure

The amide open chain ligands are a well suited type of antenna for lanthanide(III) ( $\text{Ln}$ ) ions, because they could shield the encapsulated lanthanide ion from interaction with the surroundings effectively, and

thus to achieve strong fluorescent emission of metal ions<sup>[1-7]</sup>. Up to now, a large amount of  $\text{Eu}(\text{III})$  and  $\text{Tb}(\text{III})$  complexes bearing such type of ligands have been widely investigated primarily due to their good

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luminescent properties<sup>[8-9]</sup>. Recently, our previous work has demonstrated that the Sm(III) and Eu(III) complexes with *N*-phenyl-2-(5-chloro-quinolin-8-yl)acetamide exhibit the characteristic emission of the Eu(III) and Sm(III) ions, respectively<sup>[10-11]</sup>. As a continuation of our research, we report here the structures of the ligands another three Ln(III) complexes (Ln=La, Tb and Dy), together with their fluorescence properties in solid state.

## 1 Experimental

### 1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra ( $\nu=4\,000\sim400\text{ cm}^{-1}$ ) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer, and in the measurements of emission and excitation spectra the pass width is 5 nm.

### 1.2 Preparations of complexes 1~3

The title Ln(III) complexes were synthesized according to the literature method<sup>[10-11]</sup>.

**1:** Colorless blocks. Anal. Calcd. for  $\text{C}_{36}\text{H}_{29}\text{Cl}_2\text{N}_8\text{O}_{13}\text{La}$  (%): C, 43.61; H, 2.95; N, 11.30. Found (%): C, 43.33; H, 3.09; N, 11.42. FTIR ( $\text{cm}^{-1}$ ):  $\nu(\text{C}=\text{O})$  1 670,  $\nu(\text{C}=\text{N})$  1 582,  $\nu(\text{Ar}-\text{O}-\text{C})$  1 174,  $\nu_1(\text{NO}_3)$  1 500,  $\nu_4(\text{NO}_3)$  1 283.

**2:** Colorless blocks. Anal. Calcd. for  $\text{C}_{17}\text{H}_{15}\text{ClN}_5\text{O}_{12}\text{Tb}$  (%): C, 30.22; H, 2.24; N, 10.36. Found (%): C, 30.20; H, 2.16; N, 10.43. FTIR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3403,  $\nu(\text{C}=\text{O})$  1 660,  $\nu(\text{C}=\text{N})$  1 571,  $\nu(\text{Ar}-\text{O}-\text{C})$  1 172,  $\nu_1(\text{NO}_3)$  1 505,  $\nu_4(\text{NO}_3)$  1 293,  $\rho(\text{O}-\text{H})$  879.

**3:** Colorless blocks. Anal. Calcd. for  $\text{C}_{17}\text{H}_{15}\text{ClN}_5\text{O}_{12}\text{Dy}$  (%): C, 30.06; H, 2.23; N, 10.31. Found (%): C, 30.19; H, 1.96; N, 10.22. FTIR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3 402,  $\nu(\text{C}=\text{O})$  1 664,  $\nu(\text{C}=\text{N})$  1 573,  $\nu(\text{Ar}-\text{O}-\text{C})$  1168,  $\nu_1(\text{NO}_3)$  1 503,  $\nu_4(\text{NO}_3)$  1 289,  $\rho(\text{O}-\text{H})$  877.

#### 1.3.1 X-ray crystallography

The X-ray diffraction measurement for complexes **1~3** were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\,073\text{ nm}$ ) by using  $\varphi$ - $\omega$  scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program<sup>[12]</sup>. The structures were solved by direct methods and refined by fullmatrixleast-square on  $F^2$  using the SHELXTL-97 program<sup>[13]</sup>. All non-hydrogen atoms were refined anisotropically. The H atoms for water molecules are located from difference Fourier map and refined with restraints in bond length and thermal parameters. All the other H atoms were positioned geometrically and refined using a riding model. SQUEEZE procedure was applied to deal with the crystal solvent molecules of the complex **1**. Details of the crystal parameters, data collection and refinements for complexes **1~3** are summarized in Table 1.

CCDC: 1438578, **1**; 1438579, **2**; 1438580, **3**.

Table 1 Selected crystallographic data for complexes 1~3

	1	2	3
Empirical formula	$\text{C}_{36}\text{H}_{29}\text{Cl}_2\text{N}_8\text{O}_{13}\text{La}$	$\text{C}_{17}\text{H}_{15}\text{ClN}_5\text{O}_{12}\text{Tb}$	$\text{C}_{17}\text{H}_{15}\text{ClN}_5\text{O}_{12}\text{Dy}$
Formula weight	991.48	675.71	679.29
$T / \text{K}$	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
$a / \text{nm}$	1.817 0(8)	1.097 8(6)	1.102 27(12)
$b / \text{nm}$	1.417 2(6)	0.881 8(5)	0.882 75(10)
$c / \text{nm}$	1.673 90(10)	2.471 5(11)	2.477 89(19)
$\beta / (^\circ)$	112.114 0(10)	111.040(19)	110.881(4)
$V / \text{nm}^3$	3.993(2)	2.233(2)	2.252 7(4)

Continued Table 1

<i>Z</i>	4	4	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.649	2.010	2.003
Unique	3 530	3 928	3 965
<i>R<sub>int</sub></i>	0.097 6	0.030 4	0.038 8
GOF	1.025	1.049	1.024
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.052 6 <i>wR</i> <sub>2</sub> = 0.058 0	<i>wR</i> <sub>2</sub> = 0.102 9 <i>R</i> <sub>1</sub> = 0.028 4	<i>R</i> <sub>1</sub> = 0.025 8 <i>wR</i> <sub>2</sub> = 0.054 0
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.086 8 <i>wR</i> <sub>2</sub> = 0.061 2	<i>wR</i> <sub>2</sub> = 0.111 9 <i>R</i> <sub>1</sub> = 0.041 1	<i>R</i> <sub>1</sub> = 0.033 6 <i>wR</i> <sub>2</sub> = 0.058 5
Largest peak and hole / (e·nm <sup>-3</sup> )	899 and -1 190	513 and -409	575 and -414

## 2 Results and discussion

### 2.1 Crystal structure of the complexes

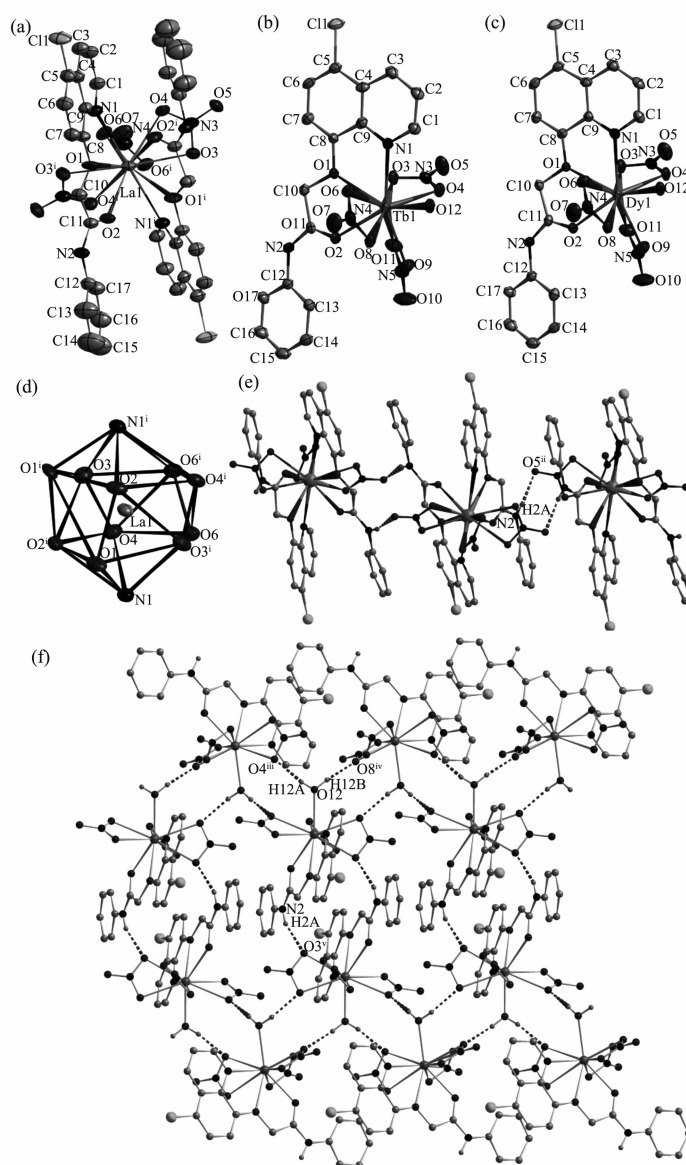
Generally, *N*-phenyl-2-(5-chloro-quinolin-8-yloxy)acetamide ligand coordinates to Ln(III) ions with molar ratio of ligand and metal being 1:1<sup>[10-11]</sup>. By contrast, it forms stable 2:1 type complex with La(III) ion. As shown in Fig.1a, La(III) ion in complex **1** is surrounded by two tridentate amide ligands with NO<sub>2</sub> donor set and three bidentate nitrate anions, thus giving distorted icosahedron coordination geometry (Fig.1d). The La-O/N bond lengths are in the range of 0.254 8(4) ~0.283 1(4) nm (Table 2), comparable to the La(III) complexes with similar donor sets<sup>[6-7]</sup>. The crystal structure of **1** is similar as that of [LaL<sup>a</sup><sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] and [LaL<sup>b</sup><sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]·H<sub>2</sub>O in our previous work<sup>[6-7]</sup> (L<sup>a</sup>=*N,N*-diphenyl-2-(quinolin-8-yloxy)acetamide, L<sup>b</sup>=*N*-

(naphthalene-1-yl)-2-(quinolin-8-yloxy)acetamide). In the crystal, pairs of intermolecular N-H···O hydrogen bonds between the amide N atoms and adjacent nitrate O atoms link the complexes into chains along *c* axis (Fig.1e).

Complexes **2** (Fig.1b) and **3** (Fig.1c) are isostructural and crystallize in the monoclinic, space group *P*2<sub>1</sub>/*c*, same as the Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Er(III) complexes with same ligand<sup>[10-11]</sup>. The center Ln(III) ion with bicapped square antiprism coordination geometry is coordinated by one tridentate L, three bidentate nitrate anions and one water molecule. Similarly, in the crystal of each complex, intermolecular O-H···O (O12-H12A···O4<sup>iii</sup> and O12-H12B···O8<sup>iv</sup>) and N-H···O (N2-H2A···O3<sup>v</sup>) hydrogen bonds link the complex into a 2D supramolecular network (Fig.1f, Symmetry codes: <sup>iii</sup> -*x*+1, *y*+1/2, -*z*+1/

Table 2 Selected bond lengths (nm) in complexes 1-3

1					
La1-O2	0.254 8(4)	La1-O3	0.267 9(4)	La1-N1	0.276 1(5)
La1-O6	0.259 3(4)	La1-O4	0.271 5(4)	La1-O1	0.283 1(4)
2					
Tb1-O12	0.232 6(3)	Tb1-O6	0.246 1(3)	Tb1-O4	0.250 1(3)
Tb1-O2	0.234 0(3)	Tb1-O8	0.249 5(3)	Tb1-O3	0.251 1(3)
Tb1-O9	0.243 0(4)	Tb1-O11	0.250 0(4)	Tb1-N1	0.254 4(4)
Tb1-O1	0.256 6(3)				
3					
Dy1-O12	0.233 1(3)	Dy1-O6	0.245 3(3)	Dy1-O4	0.249 7(3)
Dy1-O2	0.234 8(3)	Dy1-O8	0.250 2(3)	Dy1-O3	0.251 0(3)
Dy1-O9	0.241 9(3)	Dy1-O11	0.251 5(3)	Dy1-N1	0.254 7(4)
Dy1-O1	0.256 3(3)				



Hydrogen bonds are shown in dashed line; Symmetry codes: <sup>i</sup>  $-x, y, -z+1/2$ ; <sup>ii</sup>  $x, -y+1, z-1/2$ ; <sup>iii</sup>  $-x+1, y+1/2, -z+1/2$ ; <sup>iv</sup>  $-x+1, y-1/2, -z+1/2$ ; <sup>v</sup>  $-x+1, -y, -z$

Fig.1 Molecular structures of complexes **1**~**3**(a~c) shown with 30% probability displacement ellipsoids; (d) Coordination geometry of the center La(III) ion in complex **1**, atoms shown with 30% probability displacement ellipsoids; (e) Extended chain-like structure along *c* axis in complex **1** formed by intermolecular N-H...O hydrogen bonds; (f) Extended 2D supramolecular structure in complex **2** formed by intermolecular hydrogen bonds.

Table 3 Hydrogen bonds information in complexes **1**~**3**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠ D-H...A / (°)
<b>1</b>				
N2-H2A...O5 <sup>ii</sup>	0.086	0.210	0.293 8(7)	165.7
<b>2</b>				
O12-H12A...O4 <sup>iii</sup>	0.084 6(10)	0.202 6(14)	0.286 3(4)	170(4)
O12-H12B...O8 <sup>iv</sup>	0.084 7(10)	0.189 2(11)	0.273 9(4)	178(4)
N2-H2A...O3 <sup>v</sup>	0.09	0.202	0.286 7(4)	155.6

Continued Table 3

3				
O12-H12A...O4 <sup>iii</sup>	0.085 0(10)	0.203 4(15)	0.286 9(4)	167(4)
O12-H12B...O8 <sup>iv</sup>	0.084 5(10)	0.190 5(12)	0.274 9(4)	176(5)
N2-H2A...O3 <sup>v</sup>	0.090	0.204	0.288 4(5)	156.4

Symmetry codes: <sup>ii</sup>  $x, -y+1, z-1/2$ ; <sup>iii</sup>  $-x+1, y+1/2, -z+1/2$ ; <sup>iv</sup>  $-x+1, y-1/2, -z+1/2$ ; <sup>v</sup>  $-x+1, -y, -z$

2; <sup>iv</sup>  $-x+1, y-1/2, -z+1/2$ ; <sup>v</sup>  $-x+1, -y, -z$ .

## 2.2 IR spectra

The spectral regions for all the complexes are more or less similar due to the similarity in coordination modes of the ligand with the metal center. The free ligand L exhibit three absorption bands at 1 682, 1 598 and 1 241  $\text{cm}^{-1}$ , assigned to  $\nu$  (C=O),  $\nu$  (C=N) and  $\nu$  (C-O-C), respectively [10]. However, in the complexes, such bands shift evidently to lower frequency, indicating that the oxygen atoms of the carbonyl group, quinoline nitrogen atoms and etheral oxygen atoms take part in coordination to the central Ln(III) ion [3-5]. Additionally, the general pattern of the IR spectroscopy supports the normal coordination of the bidentate nitrate group [6-7]. It is in accordance with the result of the crystal structure study.

## 2.4 UV spectra

The UV spectra of the ligand L and complexes **1** ~ **3** in acetone solution ( $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) were measured at room temperature (Fig.2). The spectra of L features two main bands located around 240 ( $\epsilon = 304\ 366 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 272 nm ( $\epsilon = 169\ 788 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). The bands could be assigned to characteristic

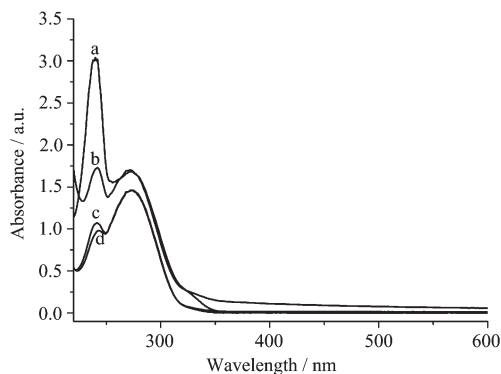


Fig.2 UV spectra of the ligand L(a), **1** (b), **2** (c) and **3** (d) in the acetone solution at room temperature

$\pi$ - $\pi^*$  transitions centered on benzene and quinoline units, respectively [6]. Similar bands can be observed in the spectra of **1** (241 nm,  $\epsilon = 174\ 235 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ; 273 nm,  $\epsilon = 168\ 132 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), **2** (241 nm,  $\epsilon = 107\ 529 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ; 273 nm,  $\epsilon = 146\ 195 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and **3** (242 nm,  $\epsilon = 98\ 529 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ; 273 nm,  $\epsilon = 145\ 803 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). However, the hyperchromicities indicate that the ligand L takes part in the coordination in all complexes.

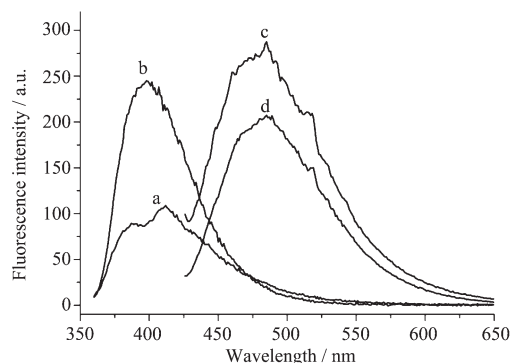


Fig.3 Fluorescence emission spectra of the ligand L (a), **1** (b), **2** (c) and **3** (d) in solid state at room temperature

## 2.4 Fluorescence spectra

The fluorescence spectra of the ligand L and complexes **1** ~ **3** have been studied in solid state at room temperature. The results show that the emission spectra of the ligand L and complex **1** exhibit similar emission peak at about 400 nm when excited at 310 nm. It also can be seen that the emission intensity of the complex **1** is much higher than that of L, which may be explained from two aspects: first, in the complex **1**, the molar ratio of the ligand and La(III) ion is 2:1; second, the coordination of La(III) ion may enhance the  $\pi \rightarrow \pi^*$  electron transition of the acetamide ligand [6]. By contrast, complexes **2** and **3** show quite different peak at about 500 nm. The

behavior of Tb(III) and Dy(III) ions coordinated to the ligand is regarded as that of emissive species resulted from a CHEF effect (chelation enhancement of the fluorescence emission)<sup>[7]</sup>.

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